Significance of the structural properties of CaO catalyst in the production of biodiesel: An effect on the reduction of greenhouse gas emissions

Radomir B. Ljupković[1], Radoslav D. Mićić[2], Milan D. Tomić[3], Niko S. Radulović[1], Aleksandar Lj. Bojić[1], Aleksandra R. Zarubica[1]

[1]*Department of Chemistry, Faculty of Science and Mathematics, University of Niš, Niš, Serbia*
[2]*NTC NIS Naftagas – Novi Sad, Novi Sad, Serbia*
[3]*Faculty of Agriculture, University of Novi Sad, Novi Sad, Serbia*

Abstract

The influence of the physicochemical properties of a series of CaO catalysts activated at different temperatures on the biodiesel production was investigated. These catalysts show dissimilar yields in the transesterification of triglycerides with methanol. We have found significant relationships between structural properties (the type of the pore system, the typical CaO crystal phase and the sizes of crystallites (up to 25 nm), the minimal weight percentage of CaO phase, the total surface basicity and potential existence of two types of basic active sites) of CaO prepared and activated by means of thermal treatment at highest temperature and catalytic efficiency. Benefits of this catalyst are short contact time, standard operating temperature and atmospheric conditions, relatively low molar ratios and small catalyst loading. These all together resulted in a very high biodiesel yield of high purity. The properties of different biodiesel (obtained with the use of the prepared CaO catalyst) blends with different diesel and biodiesel ratios indicate that the higher the fraction of biodiesel fuel the better the achieved fuel properties according to the EU standards. A significant reduction of CO_2 and CO emissions and only a negligible NO_x increase occurred when blends with an increased biodiesel portion was used. The use of biodiesel derived blends, and the eventual complete replacement of fossil fuels with biodiesel as a renewable, alternative fuel for diesel engines, would greatly contribute to the reduction of greenhouse gas emissions.

Keywords: biodiesel production, CaO catalyst, greenhouse gas emissions, structural catalytic properties.

Available online at the Journal website: http://www.ache.org.rs/HI/

The great attention has been given lately to biodiesel production from renewable energy resources (*e.g.*, vegetable oils and/or animal fats) because of energetic, ecological, geo-political and economic benefits. The production and use of biodiesel provided the means to a net reduction of CO_2, CO, NO_x, SO_x emissions, directly related to the "greenhouse effect", *i.e.*, global warming, then soot particles and unburned hydrocarbons released from diesel engines, and finally the removal of waste greases [1]. Further, it enables the usage of domestic renewable energy/fuel resources and diminishes the dependence on crude oil import. Other advantages of biodiesel use are its lubricant properties, acceptable cetane number, flash point and low temperature properties, making it an alternative, environmental friendly, biodegradable, renewable fuel [2,3], and a direction to sustainable development and economy.

Biodiesel as non-petroleum derived fuel is a mixture of fatty acid methyl or rarely ethyl esters (FAME and FAEE) obtained by catalytic transesterification of vegetable oils/fats with the two short chain alcohols. The present technology of biodiesel production comprises the utilization of homogeneous catalysts (NaOH and/or KOH) [4]. Typically, NaOH or KOH are used as base homogeneous catalysts. Disadvantages of homogeneous catalysis are the recovery of the catalyst used in the transesterification reaction and considerable volume of wastewater discharged from the process utilized to refine the dissolved alkali hydroxide from the produced biodiesel.

Despite the long history of application of homogeneous catalysis in biodiesel production, a great number of benefits of heterogeneous catalysts are recognized. The utilization of heterogeneous catalysts would be a solution for most of environmental and economic drawbacks of homogeneously catalyzed process. A heterogeneous catalyst can be easily and quickly sepa-

rated and reused and the produced biodiesel and gly-cerin could be rapidly purified and collected after sepa-ration. This easier and cheaper separation process would enable the elimination of consumption of large volu-mes of wastewaters [5]. In addition, the use of hete-rogeneous catalyst in biodiesel production makes it possible to simplify the production process by omitting sections from the complete process technology.

However, at present there is only one commercially accepted transesterification process technology. Also, heterogeneous catalysts are not consumed in the production process, whereas homogeneous processes require a fresh batch of catalyst for each new pro-duction cycle.

A number of series of basic or acidic heterogeneous catalysts (with and/or without promoters) have been investigated and used in the methanolysis of vegetable oils [6,7]. Basic heterogeneous catalysts give higher reaction rate than acidic ones and are predominantly prepared and tested. Despite the fact that several basic catalysts have exhibited promising activities, such as alkali and alkali earth oxides [8,9], alkali and alkali earth carbonates [10], basic zeolites [11], hydrotalcites [12,13] under the atmospheric pressure, no real repla-cement was found for the homogeneous process.

Among alkaline earth oxides, CaO and MgO have attracted more attention than the others due to the solubility of BaO in methanol and the tendency of SrO to react with CO_2 and water [14], and due to their dissolution in the reaction medium that makes the process a homogeneous one.

Mootabadi *et al.* [15] have investigated biodiesel production process from palm oil using alkaline earth oxides, *i.e.*, CaO, SrO and BaO calcined at 500 °C for 3 h, as the heterogeneous catalysts. The catalytic activity of the three catalysts was in the sequence of CaO < SrO < BaO. It was registered that the biodiesel yield was about 5% when CaO was used as the catalyst after 60 min of the reaction under following conditions: catal-yst/oil mass ratio 0.03, methanol/oil molar ratio 9:1. The results from the study of basicity verified that the basic strength was in the same sequence of CaO < SrO << BaO [15]. The basic properties of the catalysts were established as the major determinant for the catalytic activity among the catalysts employed in the cited work [15].

Chen *et al.* [16] have studied the basicity of the alumina-supported alkaline earth metal oxides calcined at 550 °C for 6 h (CaO/Al$_2$O$_3$ was calcined at tempe-ratures in the range: 300–750 °C). The basic properties (*i.e.*, the amount of basic sites) of alkaline earth oxides are influenced by the calcination temperature, while the strength of basic sites is not influenced by the cal-cination temperature. The calcination temperature of

550 °C yielded the highest amount of basic sites of CaO [16].

Veljković *et al.* [17] have prepared CaO catalyst by calcination at different temperatures (300, 500, 550, 600, 700 and 900 °C) for 2 h in their investigation on the kinetics of sunflower oil methanolysis catalyzed by calcium oxide. The increase of the calcination tempe-rature to a certain value caused the increase of the CaO activity; the optimal CaO calcination temperature of 550 °C was recognized. This result was explained by dehydration of Ca(OH)$_2$ and the transformation of CaCO$_3$ to CaO [16–18], and additionally by the amount of active sites [16–18]. The FAME yield of rather more than 90% was achieved by using the CaO catalyst cal-cined at 550 °C after 120 min of the reaction under the following conditions: catalyst amount, based on the oil weight, %: 1.0; average catalyst particle size, μm: 2.8; reaction temperature: 60 °C; agitation speed, rpm: 900 [17].

Granados *et al.* [18] have studied biodiesel pro-duction from sunflower oil by using the activated calcium oxide by calcinations at: 200, 500 and 700 °C. The maximal FAME yield slightly larger than 90% was obtained over CaO calcined at 700 °C after 90 min of the reaction (conditions applied: catalyst amount, 0.5 g; 50 g of oil; reaction temperature: 60 °C; agitation speed, rpm: 1000) [18]. The catalytic activity of CaO was improved by activation treatment at 700 °C after transformation of the CaCO$_3$ to CaO; the carbonate groups were established as the main catalyst surface poisoning species [18].

Cho *et al.* [19] have considered transesterification of tributyrin with methanol over calcium oxide catalysts prepared from various precursors (calcium acetate monohydrate (CA), calcium carbonate (CC), calcium hydroxide (CH), calcium nitrate tetrahydrate (CN), cal-cium oxalate monohydrate (CO)). The precursors were calcined for 2 h at a calcination temperature that was varied from 500 to 900 °C at an interval of 100 °C. The activity of the catalysts increased in the following order: CN-800 < CC-800 < CO-800 ≈ CA-800 < CH-800 [19]. The conversion of more than 90% over CH-800 in transesterification of tributyrin (TriB) with methanol was achieved under the reaction conditions: TriB/ /MeOH mole ratio = 1/6 and reactant/catalyst mass ratio = 16.4/0.010 [19]. The basicity of the prepared calcium oxide catalysts also differed according to the precursors, and the relationship between the conver-sion level and the basicity of the CH catalysts was established [19].

Kouzu *et al.* [20] have probed CaO catalyst obtained after calcination of pulverized lime stone at 900 °C for 1.5 h as solid base catalyst for transesterification of soybean oil in biodiesel production. The authors have determined that the catalytic activity was in the sequ-

ence of CaO > Ca(OH)$_2$ >> CaCO$_3$. The yield of FAME at reflux of methanol was 93% for CaO, 12% for Ca(OH)$_2$, and 0% for CaCO$_3$ [20]. The basicity of catalysts seemed to be determinant for the catalytic activity among all the samples [20].

In their other work, Kouzu *et al.* [21] have examined the active phase of calcium oxide used as solid base catalyst for transesterification of soybean oil with ref-luxing methanol. The catalyst was prepared as it was previously mentioned [20]. Calcium oxide combined with the by-produced glycerol gave calcium diglycer-oxide that was a major constituent of the collected catalyst. Calcium diglyceroxide would be the active phase in the catalytic reaction with usage of calcium oxide for biodiesel production. This catalyst had the advantage of tolerance to air-exposure [21].

Wei *et al.* [22] have investigated the activity of the eggshell-derived CaO catalyst calcined at different temperatures between 200 and 1000 °C for 2 h in the transesterification of soybean oil to produce biodiesel. They have claimed that the best catalytic performance was achieved for calcination temperature above 800 °C when XRD patterns showed a crystalline CaO phase. CaO was the active phase of the eggshell derived catal-ysts [22]. When the calcination temperature was 700 °C, a yield of 90% was achieved. One the other side, the experimental results showed that a 9:1 molar ratio of methanol to oil over 3 wt.% of eggshell-derived catalyst (calcined at 1000 °C), 65 °C reaction temperature gave the biodiesel yield that exceeded 95% at 3 h [22].

To the best of our knowledge, there is no complete consensus on different activation procedures applied in the preparation of CaO-based catalysts published and on the relevance of the physicochemical properties of catalysts for beneficial catalytic performances. Addi-tionally, there are no data on the potential effect of the use of pure biodiesel obtained over CaO and/or diesel––biodiesel blends on the CO$_x$ and NO$_x$ emissions. Espe-cially, such data concerning investigations in Serbia are missing in the scientific literature. Thus, in this work we decided to rectify this situation and investigate an im-pact of structural characteristics of CaO catalyst on the efficiency in the transesterification reaction, and a potential effect of biodiesel usage on the diesel engine performances and greenhouse gases emission.

EXPERIMENTAL

Preparation of catalyst, materials selection, standard characterization of feedstock and fuel

Calcium oxide of technical grade was used as the catalyst precursor. It was further calcined at selected temperatures (500, 750 and 900 °C) for 2.5 h under static air in order to prepare pure CaO-based activated catalysts. After calcination, the CaO-based catalyst

powder was pressed into pellets. The pellets were sieved to obtain a fraction 1.0–1.5 mm in size. These fraction dimensions were optimal to avoid potential external diffusion restrictions within the reactor basket. Catalyst samples were labeled CaO-T, where T repre-sented the calcination temperature. Afterwards, the characterization of the catalysts was performed.

Methanol of HPLC grade was used in the test reactions. Sunflower oil from a domestic producer was employed in the transesterification reactions. It was selected because sunflower represents a typical oilseed plant in Serbia and the region.

The particular properties of the feedstock and the obtained biodiesel (density, kinematic viscosity, cetane index, low temperature properties, flash point, sulfur content, water content, heating value) were deter-mined by standardized methods: JUS EN 14214 (SRPS ISO 12185); JUS E K8.028 (SRPS ISO 3104); EN 14104: 2003 (SRPS ISO 4264); EN ISO 5165: 1998; EN 116; SRPS EN ISO 2719; ASTM D 5453; SRPS ISO 12937; ASTM D5865-07.

Catalysts characterization

Textural features of CaO catalytic samples were studied by low temperature N$_2$ adsorption/desorption method using a Micromeritics ASAP 2010 instrument with He as the carrier gas. Specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equa-tion, pore size distribution was estimated based on the Barrett–Joyner–Halenda (BJH) method, and the ave-rage pore diameter was determined as the BJH desorp-tion mean pore diameter.

X-ray diffraction analysis (XRD) was conducted in order to determine the crystal structure of the CaO--based catalysts on an XRD Philips APD-1700 diffracto-meter with a Cu-anticathode and monochromator (at 40 kV and 55 mA). Crystallite sizes were calculated from the Scherer equation.

Thermogravimetric (TG) and differential thermal analyses (DTA) were done on a Baehr STA 503 appa-ratus in inert atmosphere. The measurements were performed in the temperature range 25–1000 °C using a heating rate of 10 °C/min.

Surface properties were revealed by FTIR spectros-copy on a Win Bomem 1000 instrument in the region 4000–400 cm^{-1}. Before the recordings, the catalyst samples were exposed to phenol vapors to investigate the basic nature of surface sites, and afterwards exposed to vacuum to remove any physically adsorbed vapors.

Morphological properties of the bulk catalysts were determined by a scanning electron microscope (SEM, JOEL JSM-6460 L), at different magnification (up to 100000×) at the accelerating voltage of 25 kV.

Catalytic test, biofuel products profile determination

Transesterification of sunflower oil was conducted over the prepared CaO catalysts in a stirred, commercial reactor, Parr 4520. The catalyst loading was 1 wt.% relative to the total reagents weight, the methanol to oil ratio 6:1 (*w/w*), at reflux conditions of methanol, and mixing rate of 250 rpm. Constant reaction temperature (64 °C) was maintained during 5 h of the reaction run at atmospheric pressure. Reaction products samples were taken after each 1 h of a single reaction run. The batch reactor was heated to the desired temperature with a constant ramp of 5 °C/min starting from ambient temperature, and the zero reaction point was the moment when the desired temperature was reached.

Reaction products, as well as the oil profile, were characterized by gas chromatography (GC HP 5980 Series II with a FID detector) in accordance with the standard procedure given by SRPS EN 14103. Methyl heptadecanoate (>99%, Fluka Co.) was used as the internal standard in quantitative analyses, and a standard mixture of methyl esters in qualitative analyses. The following conditions of the GC analyses were employed: 30 m long capillary column, the flow of 2 ml/min of He as the carrier gas, and the analyte separation isothermally at 210 °C during 10 min. Catalyst activity was ranked as FAME yield calculated as we have reported in our previous work [23].

Engine performances and exhaust gases emissions

Engine performances were investigated on a Tractor type Mahindra 6500. This type of tractor is common in Serbia, and can be used for various purposes in agriculture. The conventional working conditions of the tractor engine with four cylinders (Tier of the second generation) were reached during the investigation: rated power of 48.4 kW at 2200 rpm, compression ratio of 19.5:1, maximal torque of 217.4 Nm. Fuel injection pressure 250–260 bar was used inside the pump MICO Bosch (VE type).

Fuel consumption was determined by the volume--method applying a flow-meter of type Pireburg 2911. Exhaust gas emissions were resolved according to the standard ISO 8178-4 and tracked with the use of Testo 355 portable analyzer.

RESULTS AND DISCUSSION

Structural properties of the CaO catalyst

The textural properties of the prepared catalysts (BET surface area, average pore diameter, BJH cumulative desorption pore volume and maxima in pore size distribution (PSD)) are shown in Table 1. These properties are important characteristics of the solid state CaO-based catalysts because they readily influence the catalytic efficiency in the transesterification of sunflower oil. These catalytic properties are also in correlation with the precursor of the CaO catalyst and thermal history of the activated CaO-based catalyst samples.

Specifically, the increase of the calcination/activation temperature of the CaO catalyst samples has caused a slight decrease of BET surface areas from 5.2 to 4.1 m^2/g and simultaneously an increase of the average pore diameters (Table 1). Accordingly, the mean pore diameter became greater with the increase of the calcination temperature from 500 to 900 °C. Therefore, the sintering process went on to a smaller extent and this probably resulted in a consolidation of the catalyst samples [24].

In this study, the measured specific surface areas of the CaO catalysts had somewhat lower values of BET surface areas when compared to the results of other authors [18,25]. These results may be explained by the fact that the exact origin of the CaO catalysts was unknown, thus, the catalyst features could be completely different despite the comparable gross chemical composition. In addition, we believe that the BET surface area of the CaO catalyst should be correlated with the precursor type and the relevant thermal treatment applied. To the best of our knowledge, there are no reported data on an identical CaO precursor used; hence, no analogous results on the textural properties of CaO catalysts could be expected.

The results indicate that the CaO catalyst samples calcined at the lowest temperature possess a surface area of 5.2 m^2/g and a mean pore diameter of 11.9 nm (Table 1). The corresponding properties of the catalyst samples calcined at higher temperatures (750 and 900 °C) changed but not to a substantial extent. It seems that the textural characteristics of the CaO catalyst samples used in this experiment (from CaO-500 to CaO--900) are favorable for a liquid–solid heterogeneous phase reaction, and provide sufficient reaction surface area for the conversion of large triglyceride molecules.

Table 1. Specific surface areas, average pore diameters, pore volumes and maxima in pore size distribution for CaO-based catalysts

Catalyst	BET surface area, m^2/g	Average pore diameter, nm	BJH pore volume, cm^3/g	Maxima in PSD, nm
CaO–500	5.2	11.9	0.010	10–20; 60–140
CaO–750	4.7	12.7	0.017	12–20; 60–140
CaO–900	4.1	13.8	0.021	13–20; 60–140

Nitrogen isotherms and pore size distribution curves for the CaO-500 catalyst sample are shown in Fig. 1. The N$_2$ isotherms exhibited a typical *s*-shape behavior of IV-type with a type-H1 desorption hysteresis loop that indicated a potential presence of relatively wide cylindrical pores. The pore system is in the mesopores range between 10 and 100 nm with an average pore diameter around 28 nm according to the BJH desorption isotherms. Based on the PSD curve, a smaller fraction of the surface area is occupied by pores of around 10 nm in size followed with a larger volume fraction of pores of relatively large size between 60 and 140 nm. Such mesopores and near-edge mesopores–macropores are generated as a result of residual areas among particles formed during the catalyst preparation. The IV-type of isotherms is recognized for catalytic materials with porous system in the mesopore range [26] that additionally coincided with a rather spongy-like morphology of CaO particles proved by SEM.

The mentioned two maxima in the PSD curve may be significant during the catalytic run due to an effective mass transfer process in the conversion of relatively large triglyceride reactants. Taking into account that the approximate dimensions of triglycerides along the fatty acid chain (around 2.5 nm based on the dimension of the extended methyl oleate molecule) [18] are several orders of magnitude smaller than the meso––macropores sizes in CaO catalysts, any internal diffusion restrictions cannot be expected.

In the case of catalytic samples calcined/activated at higher temperatures only slight shifts of maxima in the PSD curves towards bigger mesopores were observed (not shown). Therefore, the increase of calcination temperature caused a shift of pore diameters to somewhat higher values for the CaO-based catalysts.

Based on these and reported CaO textural properties, the authors believe that the reactivity of the catalyst is indirectly proportional to the specific surface area, whereas it is in a direct relation with the average pore diameter [27]. Precisely, the pore diameter and/or pore volume play important roles in exhibiting the catalytic efficiency. We strongly believe that these catalytic properties are vital in expressing the catalytic activity, but not the key ones.

XRD patterns of thermally untreated commercial CaO-precursor, and CaO catalyst samples calcined at different temperatures, are given in Fig. 2. The non-calcined starting CaO precursor sample shows X-ray diffraction peaks characteristic for three different crystal phases: CaCO$_3$, CaO and Ca(OH)$_2$. The intensities of the XRD peaks, as well as their volume fractions attributed to CaO and Ca(OH)$_2$ phases, are comparable whereas the intensity of the corresponding CaCO$_3$ peak is considerably lower although still a significant one. The presence of these three crystal phases in the inactivated CaO starting material is related to its chemical composition, present impurities and potential surface interactions with CO$_2$ and/or humidity in ambient conditions.

The activation procedure through a thermal treatment of the CaO starting sample has caused a decomposition of the precursor used. The XRD pattern of CaO-500 catalyst reveals the peaks of the above-mentioned phases but now where the CaO phase is the principal one, while CaCO$_3$ and especially Ca(OH)$_2$ phases are only detectable having a volume fraction much lower when compared to the CaO phase. The hydroxide is reported to exhibit slight reactivity [28] but the carbonates are known to have no activity [20] in the transesterification reaction of soybean and rapeseed oils. Some previous work states the formation of calcium oxide at the calcination temperature of 800 °C from the
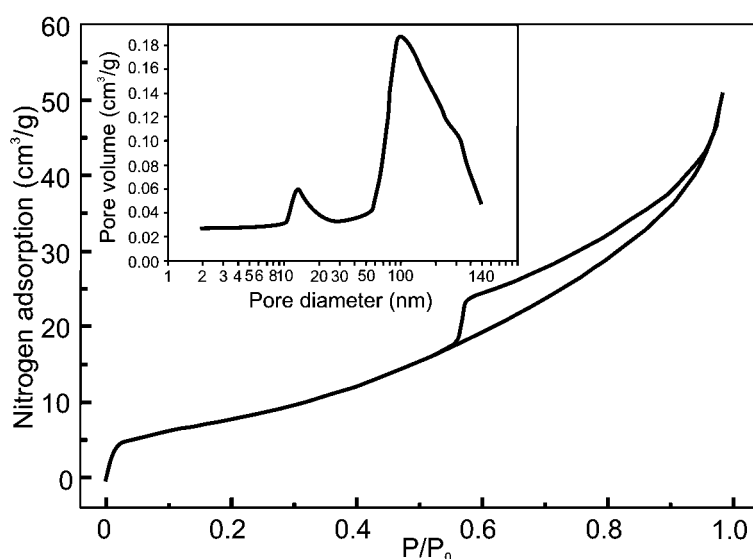

Fig. 1. N$_2$ Adsorption–desorption isotherms and pore size distribution for CaO-500 catalyst.
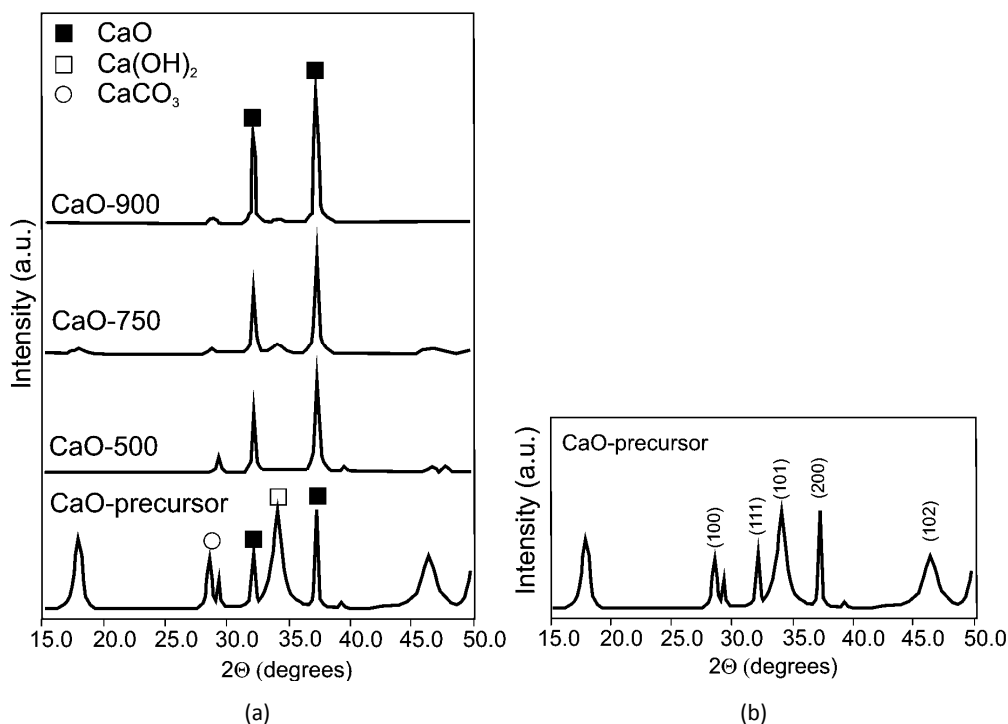
Fig. 2. XRD Patterns for CaO-based catalyst samples: a) CaO-T catalysts samples and b) CaO-precursor.

precursors [29], but we noted a CaO genesis at temperatures lower than 750 °C. Consequently, since the CaO phase may be an essential one for the catalytic activity in biodiesel production [23], it can be expected that a pure CaO catalyst would show a favorable efficiency in the transesterification of sunflower oil.

X-Ray diffraction peaks of the CaO-750 and CaO-900 catalyst samples showed the existence of a pure CaO crystalline phase. The intensity of the typical peaks of the CaO phase is higher when higher activation temperatures were used. These changes in intensity and peak width may indicate somewhat larger dimensions of the CaO crystallites formed at higher activation temperatures (Table 2). Based on the recognized crystalline phases (pure CaO) and crystallite sizes in CaO-catalyst samples calcined at higher temperatures, starting at 750 °C, we can conclude that there is a necessity to activate the CaO-based catalyst by a thermal treatment before its usage. This observation is in agreement with those of other authors [30].

The structural properties of the CaO-based catalysts (Fig. 2 and Table 2) indicate that the catalytic activity in the transesterification reaction of sunflower oil will take the following order: CaO > Ca(OH)$_2$ > CaCO$_3$. Thus, the catalysts activated at temperatures over 700 °C would perform with a significantly better catalytic efficiency as proven by our results in the test reaction.

The DTA curves of the CaO-based catalytic samples show three relatively broad endothermic peaks (Fig. 3). The first endothermic process occurring to about 120 °C was due to the removal of surface adsorbed and/or chemisorbed water and amounted to a weight loss of 5–15% depending on the particular catalytic sample. The second process was complete up to 430 °C and can be assigned to the dehydration of Ca(OH)$_2$ (Eq. (1)). The third thermal transition at 530–640 °C probably corresponded to the decomposition of CaCO$_3$ (Eq. (2)) formed by a reaction of CaO with CO$_2$ from the atmosphere. The maximum of these three peaks was positioned at somewhat lower or higher temperatures for each catalyst sample:
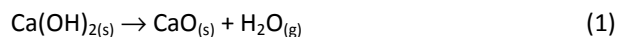
$$Ca(OH)_{2(s)} \rightarrow CaO_{(s)} + H_2O_{(g)} \tag{1}$$

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \tag{2}$$

Table 2. Crystal phases and crystallite sizes

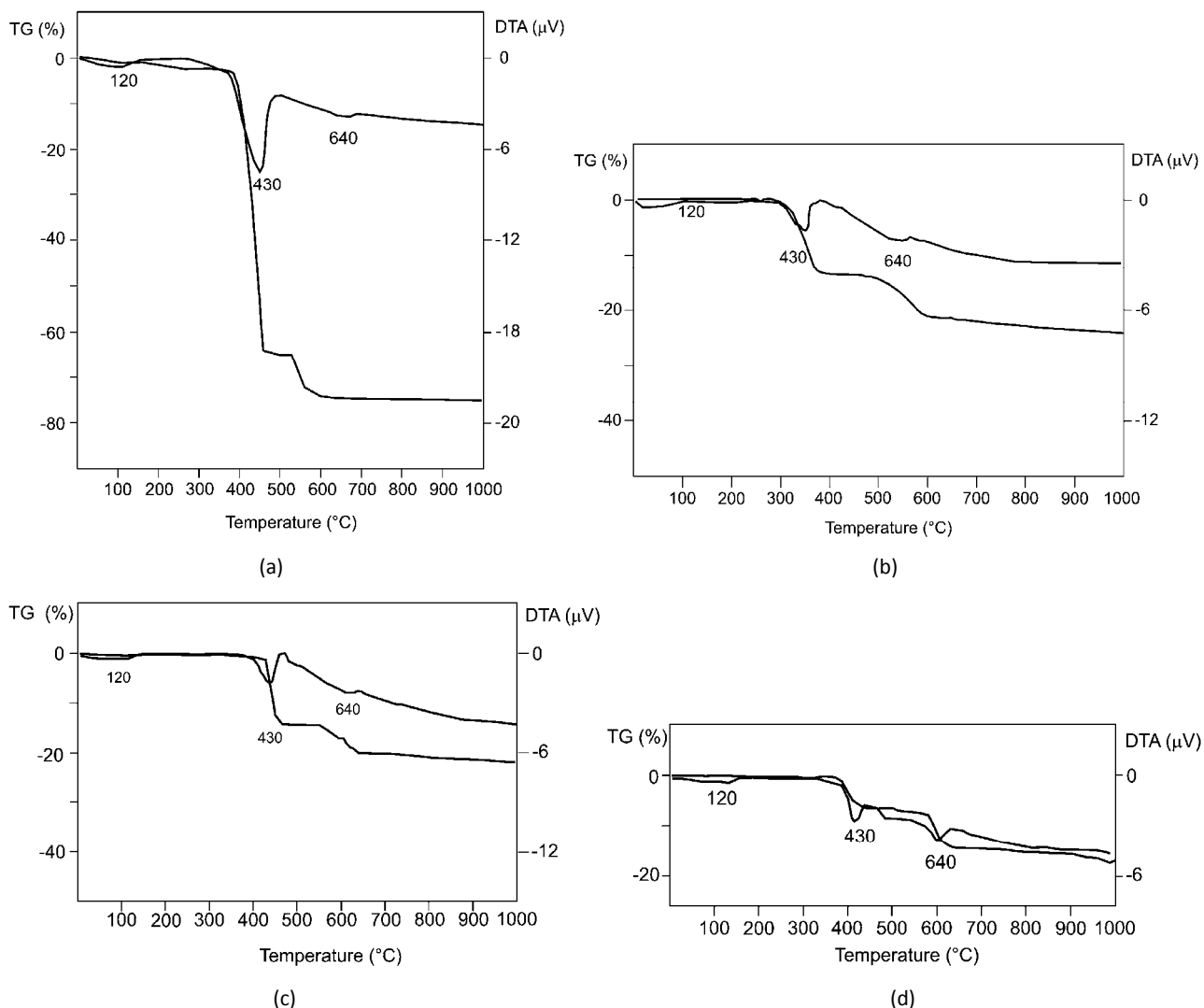| Catalyst	Crystal phases detected	Crystallite size of CaO at 37.4 °C, nm
CaO-precursor	CaO, Ca(OH)$_2$, CaCO$_3$	38.5
CaO-500	CaO, CaCO$_3$	25.5
CaO-750	CaO	25.6
CaO-900	CaO	25.7

Fig. 3. TG and DTA curves of CaO-based catalyst samples: a) CaO-non-calcined, b) CaO-500, c) CaO-750 and d) CaO-900.

Calcium hydroxide and carbonate might have been present in the starting CaO-precursor material and/or could have formed during the catalyst preparation and testing in ambient conditions. The temperatures of thermal transitions and/or decompositions are somewhat lower than those reported earlier [25,31].

However, it is obvious that the decomposition temperatures of calcium hydroxide and carbonate are shifted to higher temperatures in parallel to the increase of the catalyst activation temperature. This is in line with the thermal stabilization of the catalytic material based on CaO. Additionally, TG curves show three weight losses corresponding to desorption of the physisorbed water onto the catalyst surface, then the mentioned dehydroxylation and decarbonization processes. The percentage weight loss related to the hydroxide degradation is significant only for the non-calcined CaO catalyst sample (around 65%), where the weight percent of carbonate is around 8%. It is clear that as the temperatures of calcination are higher smaller weight percentages of

calcium hydroxide and carbonate are expected in the CaO-catalyst samples.

Based on the thermogram (Fig. 3), it seems that the weight percentage of the hydroxide in the CaO-500 sample is 10–15%, and of the carbonate about 5%. CaO samples calcined at higher temperatures possess much lower amounts of the hydroxide and carbonate. These results are consistent with the reported XRD results (Table 2 and Fig. 2). Namely, calcium hydroxide and calcium carbonate phases were detected in the non-calcined CaO sample, and only a small amount of the carbonate phase was registered in the CaO-500 sample (about 5.0% based on the TG results). This can be expected bearing in mind that the chemical species present in weight percentages lower than 5% cannot be seen in XRD patterns. Hence, the obtained XRD and TG/DTA results are entirely in agreement.

We believe that the purity of the CaO catalyst is the most important single factor determining the catalytic activity in the transesterification reaction of sunflower

oil, but we also think that small amounts of $Ca(OH)_2$ and $CaCO_3$ (less than 5%) would not significantly negatively influence the efficiency of the catalyst. However, some authors have given a stricter opinion on the deactivation of CaO-based catalysts with regard to the existence of calcium carbonate in the catalysts. They also claim a negligible catalytic activity in the presence of the hydroxide [20,28]. Namely, after an atmospheric calcination of CaO catalytic samples, deactivation of these CaO catalysts was reported by exposure to air and adsorption of CO_2 [32].

CaO catalytic samples calcined at different temperatures were analyzed by FTIR before and after being exposed to phenol vapors. This was carried out to determine the basic nature of the CaO catalyst, a relevant catalytic property for the transesterification of sunflower oil. Phenol, a rather weak acid, was selected to be the test compound for the estimation of the (active) basic catalytic sites on the catalyst surface [33]. Differences in the FTIR spectra of phenol adsorbed onto CaO surfaces of the catalytic samples differently thermally (pre)treated were observed (Fig. 4). Phenol can interact with basic sites from the catalyst surface via a dissociative adsorption giving probably $C_6H_5O^-$ [34] depending on the presence and strength of the basic catalytic sites. Thus, phenol can be physisorbed molecularly onto the framework of oxygen atoms and/or chemisorbed in the form of phenolate ions.

Vibration bands in the region 1270–1150 cm^{-1} are assigned to OH-groups directly bonded to the phenolic aromatic ring [35]. These vibration bands were detected in the FTIR spectra of the CaO catalyst samples treated at lower temperatures (500 and 750 °C). The clear pre-

sence of this vibration in the FTIR spectrum of the CaO--500 sample and also vibrations of smaller intensity in the spectrum of the CaO-750 sample indicated the possible physisorption of phenol in molecular form. We propose that such phenol adsorption may be related to the existence of one specific type of basic sites of relatively low strength. On the other side, the complete absence of this band in the spectrum of the CaO-900 catalyst indicated a probable dissociative adsorption of phenol onto basic sites of the strongest strength and/or other types of basicity. We presume that a deprotonating of phenol on the strong basic sites has occurred leading to a production of phenolates connected with metal oxide surface cations. Our findings are comparable to those previously reported the minimal calcination temperature for the genesis of the maximum amount of electron donating sites/basic sites on the CaO surface is 700 °C [36]. In our experiments this temperature was somewhat higher, *i.e.*, 750 °C.

Greater intensities of vibration bands of OH-groups (around 1650 cm^{-1}) originating from physisorbed water in CaO samples calcined at lower temperatures (500 and 750 °C) indicated that greater volumes of moisture interacted with CaO prior to calcination. These data are consistent with the TG results.

The FTIR bands at about 1475 and 1075 cm^{-1}, assigned to symmetric and asymmetric stretching vibrations of the O–C–O bonds of unidentate carbonate [18], are observable in the CaO samples calcined at lower temperatures (CaO-500 and CaO-750). Higher intensity of these stretching vibrations was observed for the CaO-500 catalyst. The lack of these bands in the CaO-900 catalytic sample corroborates no carbonate or a neg-
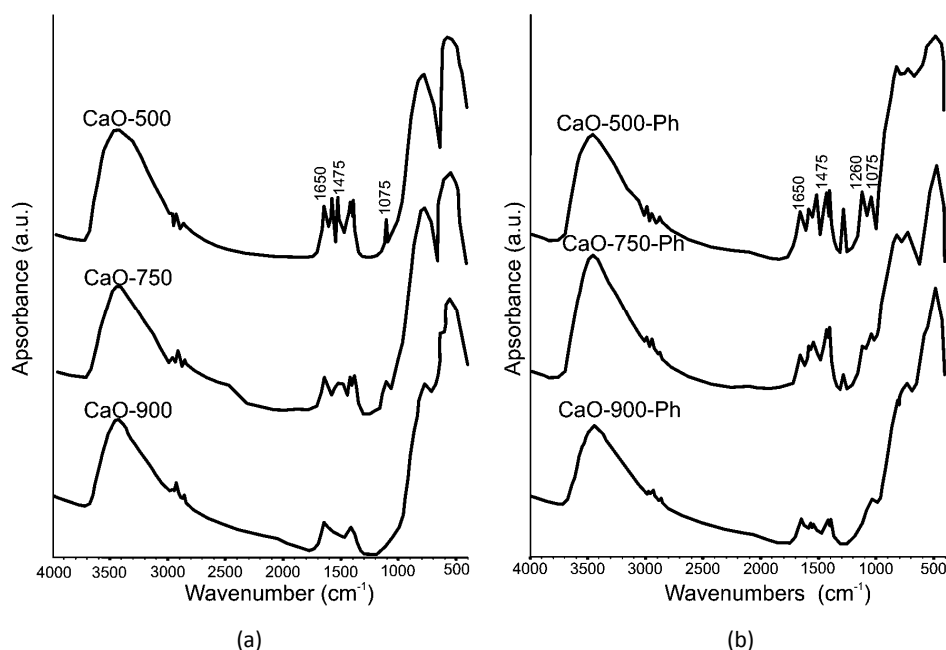

Fig. 4. FTIR Spectra of CaO-based catalyst samples: a) fresh CaO-T catalysts and b) CaO-T catalysts with (pre)adsorbed phenol.

ligible amount of carbonate on the CaO surface. All of this is in accordance with our TG/DTA results (Fig. 3).

SEM images of the CaO catalyst samples show that particle sizes decrease while pore sizes increase after thermal activation (Fig. 5). Non-calcined CaO sample possesses less defined greater particles at the surface surrounded with pores small in size. On the contrary,

Catalyst structure–activity relationships

The transesterification reaction is most often performed at atmospheric pressure, and the heating is consequently limited by the refluxing temperature of the used alcohol. Thus, the reaction temperature cannot be higher than of the boiling point of methanol.
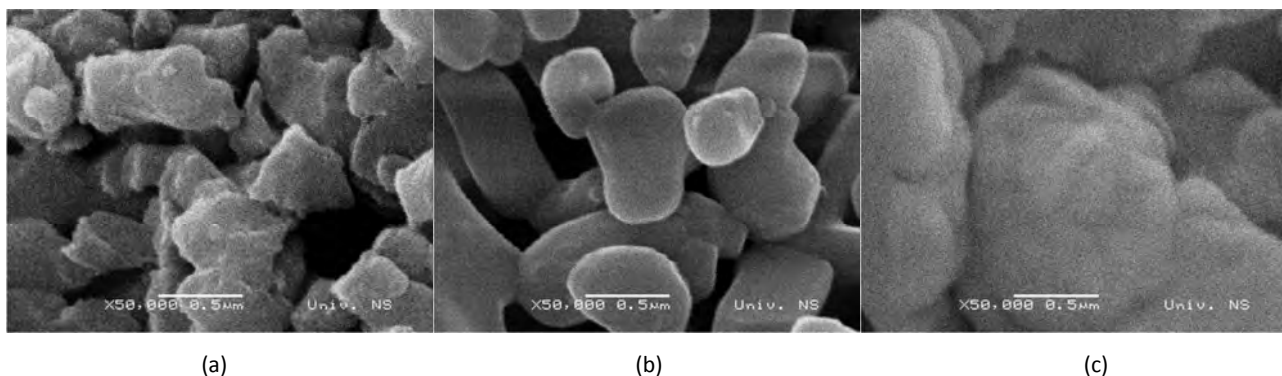

(a)   (b)   (c)

Fig. 5. SEM Images of the non-calcined CaO (a), CaO-500 (b) and used CaO-900 (c).

after the calcination at 500 °C, well defined crystallites of nano-size dimensions were observed whereas larger pores were revealed. These results are consistent with the obtained XRD data on the existing crystal phases and calculated crystallites sizes (Table 2). Such a developed pore system may provide no internal diffusion restrictions for the triglycerides molecules to interact with the catalytically active sites. After the reaction, a coalescence of the catalytic material occurred, and CaO particles were (re)organized in aggregates in a cakes-like sticky structure. These changes in the catalyst bulk morphology led to a deactivation of the catalyst by blocking the contact between the active catalytic sites and the reactants.

If an extensive evaporation of methanol occurred, this would result in a considerable decrease of FAME yield.

Figure 6 presents the fatty acids methyl esters yield, as the function of time-on-stream at atmospheric pressure and temperature of reflux of methanol over the CaO catalysts activated at different temperatures.

The maximum FAME yield of more than 90% (up to 93%) was achieved over CaO-900 catalyst after only 2 h long reaction run. Afterwards, a steady-state was established and maintained during the next 4 h of the reaction progress. A twice lower FAME yield was obtained after as long as 5 h over the CaO-750 catalyst and finally an unsatisfactory FAME yield of 18% was noted for a 5 h long run over the CaO-500 catalyst.
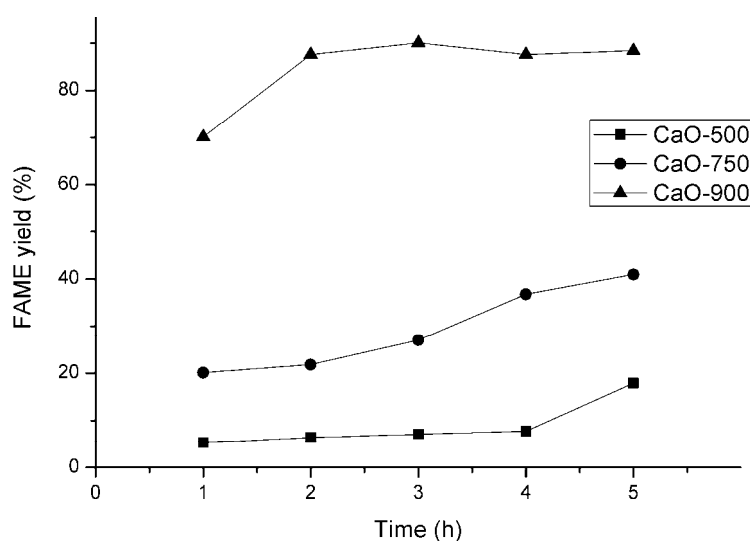

Fig. 6. FAME Yields as a function of time-on-stream over CaO-T catalyst samples.

This is an indication that the establishment of the steady-state is rather slow over CaO-catalysts activated at both lower temperatures. The reason for this is probably in an induction period necessary for the genesis of the catalyst active phases [20,37] followed by the increase of reaction rate and/or FAME yield with the more intense penetration of the reactants to the active sites during the course of biodiesel production.

The catalytic activity of CaO increased with increasing the calcination temperature (Fig. 6), and the optimal CaO calcination temperature was 900 °C in our work, that agreed with the results reported by Kouzu et al. [20,21]. These authors reported that the basicity of catalysts was essential for the catalytic activity. On the other side, we assume that not only the basicity, but adequate balance of specific surface area and pore system, presence of CaO active crystal phase with crystallites of critical dimensions, the total basicity and two types of basic sites are all necessary for the optimal catalytic efficiency. Additionally, we predict that these physico–chemical parameters of the catalysts are influenced with the calcination temperature.

Our results on the optimal calcination/activation temperature were different comparing to the results of some authors [15–19,22]; the reason may be in a fact that precursors of the CaO-based catalysts were various comparing to the compound used in this experiment. Moreover, in our case, the calcination temperatures below 900 °C were not enough high to cause formation of active crystal phase and activation of surface basic sites, while temperatures over 900 °C may induce undesirable sintering of the catalytic material, hence, changes in surface morphology and particle sizes.

A comparison of the textural, thermal, structural, acid–base and morphological properties of the catalysts differently thermally activated along with their observed efficiency suggests that physicochemical properties of the catalysts have a profound influence on the final catalytic performance in the transesterification reaction. We have found a straightforward relationship between the type of the pore system, the typical CaO crystal phase and the sizes of crystallites (up to 25 nm), the minimal weight percentage of CaO phase in the final catalyst, and the total surface basicity related to the catalytic activity.

Firstly, there is a direct link between the catalyst specific surface area and the catalyst activity; however, this property is not crucial for the onset of the catalytic activity. Namely, mesopores and near-edge meso–macropores may be of vital importance in the contact of triglycerides and catalytic active sites. The CaO crystal phase with no more than 5% of the hydroxide and carbonate exhibited very high catalytic activity. Calcinations at higher temperatures resulted in the formation of a higher number of CaO crystallites in the catalyst matrix influencing the density of basic sites required for a catalytically active site.

We wish to draw attention to the potential existence of two types of basic active sites: very strong basic sites (phenolates adsorbed), and rather less strong basic sites (phenol adsorbed). Finally, we believe that the strength of a surface base site plays a vital role in the catalyst efficiency.

The use of conventional diesel fuel and biodiesel fuel blends. Fuel properties, engine performances and exhaust gas emissions

A conventional commercial fossil-based diesel fuel was used for the comparisons with biodiesel fuel blends in order to estimate engine performances and exhaust gas emissions. In addition, a type of low sulfur diesel fuel (LSCDF) (originating from the Refinery–Novi Sad) was also selected for the assessment of the engine working performances, NO_x and CO_x emissions. Biodiesel produced over the CaO catalyst activated at 900 °C from sunflower oil was blended with commercial diesel fuel in different ratios. The selected biodiesel blends were: B25 containing 25% of biodiesel and 75% of diesel, B50, B75, and finally B100 (pure biodiesel fuel). Blends even with 25% of biodiesel are expected to affect exhaust gas emissions and improve fuel properties (Fig. 7 and Tables 3 and 4) based on the previously published report of the data that only 2% of biodiesel in a blend may influence reduction of exhaust gas emissions and some fuel properties [38]. B100 may also provide the mentioned benefits (Tables 3 and 4) and a complete replacement of diesel fuel with biodiesel might be possible if biodiesel becomes available in adequate volumes and at acceptable costs on market [38,39].

The herein laboratory obtained biodiesel (B100) fuel possessed better fuel properties than the LSCDF fuel sample with all of the properties being in the allowed limits (Table 3). Namely, especially the cold filter plugging point (CFPP) of B100 was much closer to the limited value than that of LSCDF fuel, sulfur content was one order of magnitude lower for the B100 fuel sample, and finally the cetane index (CI) was considerably higher for the B100 fuel in comparison to that of LSCDF. CI and CFPP properties of diesel derived fuels are essential parameters that are strictly determined by the fatty acids composition of the feedstock. The measured CI of B100 was higher than the standard value (50-51) and this can be related to the high content of unsaturated fatty acids (oleic and linoleic ones, up to 87%). Conversely, the CFPP value determined could be associated with the amount of mono-unsaturated fatty acids in the feedstock where oleic acid is the most important one dissolving the saturated esters [40].
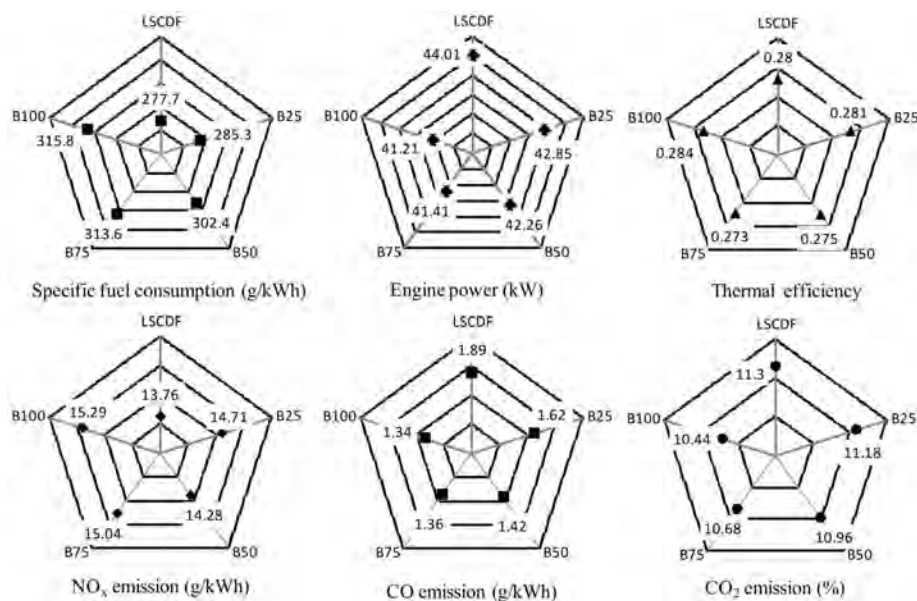
Fig. 7. Greenhouse gas emissions and engine performances.

Table 3. Fuel properties of biodiesel and LSCDF

Fuel property	Unit	Standard value	Value	
			B100	LSCDF
Flash point	°C	Min. 101	154	65
Cold filter plugging point	°C	Max. −5	−4	−19
Sulfur content	mg/kg	Max. 10	0.81	8.2
Water content	mg/kg	Max. 500	279	60
Cetane index	−	>51	51.8	49.7
High heating value	MJ kg^{-1}	−	40.35	46.29

Table 4. Selected fuel properties of biodiesel blends

Fuel property	Unit	Value		
		B25	B50	B75
Density 15 °C	kg/m^3	849.7	861.1	872.6
Viscosity	mm^2/s	3.21	3.44	3.68
Flash point	°C	98	114	132
Sulfur content	mg/kg	6.4	4.5	2.7
Water content	mg/kg	171	219	253
High heating value	MJ kg^{-1}	44.83	43.29	41.70

The properties of different biodiesel blends (Table 4) obtained from the same feedstock and the use of the herein developed CaO-based catalyst but with different diesel and biodiesel ratios indicate that the higher the fraction of biodiesel fuel the better the achieved fuel properties are when compared to the EU established standards [41]. This especially stands for the lower sulfur content, higher viscosity and flash point of the biodiesel blends. These properties are directly linked to the fraction of biodiesel blended in each particular fuel sample.

CO$_x$ and NO$_x$ – "greenhouse gas" emissions

Greenhouse gas emissions (GHGE) for the LSCDF and biodiesel blends are shown in Fig. 7. Increased biodiesel share in particular fuel blends greatly reduced CO$_2$ emissions. This is easily explainable by the lower content of carbon in biodiesel compared to its content in diesel fossil fuel (Fig. 7). On the other hand, the mentioned reduction leads to a decrease in fuel combustion efficiency. The main reason for such decrease in the combustion efficiency is the higher kinematic viscosity of the higher content biodiesel blended fuel samples.

The increase of kinematic viscosity on low scale may positively affect engine performances, but in general, it has a negative effect on the combustion quality. Viscosity is an important parameter that determines the quality of diesel fuel and its capability to atomize, as well as the smoothness of the injection into the engine, especially at lower temperatures.

The studied increase of biodiesel content in particular blends caused a reduction of CO emissions as well (Fig. 7). The highest CO emission was registered for the LSCDF whereas the lowest one was observed for the B100 fuel sample. One of the reasons for this reduction is the mentioned increase of kinematic viscosity. Another reason might be that biodiesel fuel possesses higher oxygen content that may contribute to a more complete combustion process.

On the side, the rise of the biodiesel fraction in certain blends has caused an increase of NO_x emissions to some extent (Fig. 7). NO_x emissions also grow as the temperatures of the combustion products increase. NO_x emission could be conditioned by the combustion temperature, peak pressure, process time and oxygen concentration. It is most probably in line with properties of the feedstock used for biodiesel production.

Our results on GHGE demonstrated the reduction of CO_2 content for 7.60%, and 29.10% for CO, and finally the increase in NO_x emissions for 11.12%. It is generally known that these gases contribute to global warming. We strongly believe that if renewable energy sources would be used in the future, and especially for transportation, GHGE emissions would be reduced even further. Similar observations and expectations were reported earlier on the production and use of biodiesel in Asia [38,42].

The use of LSCDF resulted in an engine power of 44.01 kW at 2200 rpm. The prepared and tested B25--100 fuels gave power from 42.85 to 41.21 kW, respectively (Fig. 7). The density of fuel samples prepared by blending biodiesel with fossil diesel increased with the addition of biodiesel. A slight increase of kinematic viscosity can positively affect engine working performances [43].

The lowest specific fuel consumption was observed for LSCDF, whereas an increase was experienced with an increase of the biodiesel portion in the blends. Therefore, B100 sample displayed the highest specific fuel consumption (Fig. 7). Such an increase could be explained by the lower heating value and higher fuel density of blends with higher amounts of biodiesel.

All tested biodiesel blends possessed higher thermal efficiency than the LSCDF sample (Fig. 7). Despite the reduced heating value and increased specific fuel consumption, the thermal efficiency was increased for all fuel samples with high biodiesel content, which enables more complete fuel combustion in the engine.

The higher cetane number causes a shorter delay in fuel combustion leading to a longer time for the complete combustion [43].

CONCLUSIONS

Calcium oxide prepared and thermally activated at higher temperatures has exhibited itself as a very effective catalyst in short run transesterification reactions of refined sunflower oil with methanol to yield biodiesel. Benefits of this catalyst are short contact time (up to 2h), standard operating temperature and atmospheric conditions, relatively low molar ratios and small catalyst loading. These all together resulted in a relatively high fatty acids methyl esters yield.

A number of key physicochemical features of the CaO catalysts – the great specific surface area and average pore diameter, almost exclusive presence of CaO crystal phase with crystallites up to limited dimensions, the total amount of surface basic sites and the two types of basic active sites – were found to be the reasons for the observed high catalytic efficiency.

The following conclusions can be reached from the comparative use of fossil diesel fuel and biodiesel blends: biodiesel fraction increase in a particular blend leads to a reduced engine power that resulted in a lower heating value and higher viscosity; the specific fuel consumption increases with the increase of the biodiesel fraction; thermal efficiency slightly increases with the increase of the biodiesel share resulting in a more complete fuel combustion; a significant reduction of CO_2 and CO emissions and only a negligible NO_x increase occurred when blends with an increased biodiesel portion was used; CO emissions diminished significantly. All these facts are consequences of better fuel combustion and take place at different engine operating regimes. More oxygen was available for burning with the increase of biofuel share due to the oxygenated nature of biodiesel; hence, decreased amounts of CO were registered in the exhaust gases.

The reduction of emissions of greenhouse gases is of vital interest due to their effect on global warming. The use of biodiesel derived blends with fossil diesel fuel, and the eventual complete replacement of fossil fuels, would greatly contribute to the reduction of greenhouse gases emissions. Further investigations on this topic and on similarly orientated ones would promote the use of biodiesel as a renewable, alternative fuel for diesel engines that could answer the energy demands and traffic transportation needs in Serbia.

REFERENCES

[1] C. Carraretto, A. Macor, A. Mirandola, A. Stoppato, S. Tonon, Biodiesel as alternative fuel: Experimental analysis and energetic evaluations, Energy **29** (2004) 2195––2211.

[2] M.S. Graboski, R.L. McCormick, Combustion of fat and vegetable oil derived fuels in diesel engines, Prog. Energy Combust. Sci. **24** (1998) 125–164.

[3] A. Srivastava, R. Prasad, Triglycerides-based diesel fuels, Renew. Sust. Energ. Rev. **4** (2011) 111–133.

[4] J. Van Gerpen, Biodiesel processing and production, Fuel Process. Technol. **86** (2005) 1097.

[5] Y. Zhang, M.A. Dube, D.D. McLean, M. Kates, Biodiesel production from waste cooking oil: 1. Process design and technological assessment, Bioresour. Technol. **89** (2003) 1–16.

[6] Y.C. Sharma, B. Singh, S.N. Upadhyay, Advancements in development and characterization of biodiesel: a review, Fuel **87** (2008) 2355–2373.

[7] G. Arzamendi, I. Campoa, E. Arguinarena, M. Snachez, M. Montes, L.M. Gandia, Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: comparisons with homogeneous NaOH, Chem. Eng. J. **134** (1997) 123–130.

[8] H.J. Kim, B.S. Kang, Y.M. Park, D.K. Kim, J.S. Lee, K.Y. Lee, Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst, Catal. Today **93–95** (2004) 315–320.

[9] T. Ebiura, T. Echizen, A. Ishikawa, K. Murai, T. Baba, Selective transesterification of triolein with methanol to methyl oleate and glycerol using alumina loaded alkali metal salt as a solid-base catalyst, Appl. Catal. A: Gen. **283** (2005) 111–116.

[10] G.J. Suppes, K. Bockwinkel, S. Lucas, J.B. Botts, M.H. Mason, J.A. Heppert, Calcium carbonate catalyzed alcoholysis of fats and oils, J. Am. Oil Chem. Soc. **78** (2001) 139-146.

[11] [11] G.J. Suppes, M.A. Dasari, E.J. Doskocil, P.J. Mankidy, M.J. Goff. Transesterification of soybean oil with zeolite and metal catalysts, Appl. Catal. A: Gen. **257** (2004) 213–223.

[12] D.G. Cantrell, L.J. Gillie, A.F. Lee, K. Wilson, Structure-reactivity correlations in MgAl hydrotalcite catalysts for biodiesel synthesis, Appl. Catal., A **287** (2005) 183–190.

[13] W. Xie, H. Peng, L. Chen, Calcined Mg-Al hydrotalcites as solid base catalysts for methanolysis of soybean oil, J. Mol. Catal., A **246** (2006) 24–32.

[14] S. Yan, H. Lu, B. Liang, Supported CaO catalysts used in the transesterification of rapeseed oil for the purpose of biodiesel production, Energ. Fuel. **22** (2008) 646–651.

[15] H. Mootabadi, B. Salamatinia, S. Bhatia, A.Z. Abdullah, Ultrasonic-assisted biodiesel production process from palm oil using alkaline earth oxides as the hetero–ge–neous catalysts, Fuel **89** (2010) 1818–1825.

[16] Y.-W. Chen, H.-Y. Chen, W.-F. Lin, Basicities of alumina-supported alkaline earth metal oxides, React. Kinet. Catal. Lett. **65** (1998) 83–86.

[17] V.B. Veljković, O.S. Stamenković, Z.B. Todorović, M.L. Lazić, D.U. Skala, Kinetics of sunflower oil methanolysis catalyzed by calcium oxide, Fuel **88** (2009) 1554–1562.

[18] M.L. Granados, M.D. Zafra Poves, D.M. Alonso, R. Mar–iscal, F. Cabello Galisteo, R. Moreno-Tost, J. Santamaria, J.L.G. Fierro, Biodiesel from sunflower oil by using activated calcium oxide, Appl. Catal. B: Environ. **73** (2007) 317–326.

[19] Y.B. Cho, G. Seo, D.R. Chang, Transesterification of tributyrin with methanol over calcium oxide catalysts prepared from various precursors, Fuel Process. Tech–nol. **90** (2009) 1252–1258.

[20] M. Kouzu, T. Kasuno, M. Tajika, Y. Sugimoto, S. Yama–naka, J. Hidaka, Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production, Fuel **87** (2008) 2798–2806.

[21] M. Kouzu, T. Kasuno, M. Tajika, S. Yamanaka, J. Hidaka, Active phase of calcium oxide used as solid base catalyst for trans esterification of soybean oil with refluxing methanol, Appl. Catal., A **334** (2008) 357–365.

[22] Z. Wei, C. Xu, B. Li, Application of waste eggshell as low-cost solid catalyst for biodiesel production, Biores. Technol. **100** (2009) 2883–2885.

[23] Dj. Vujicic, D. Comic, A. Zarubica, R. Micic, G. Boskovic, Kinetics of biodiesel synthesis from sunflower oil over CaO heterogeneous catalyst, Fuel **89** (2010) 2054–2061.

[24] G. Mekhemer, Characterization of phosphated zirconia by XRD, Raman nad IR spectroscopy, Colloids Surfaces, A **141** (1998) 227–235.

[25] Y. Tang, J. Xu, J. Zhang, Y. Lu, Biodiesel production from vegetable oil by using modifies CaO as solid basic catalysts, J. Clean. Prod. **42** (2013) 198–203.

[26] T. Liu, Y. Zhu, X. Zhang, T. Zhang, T. Zhang, X. Li, Syn–thesis and characterization of calcium hydroxide nano–particles by hydrogen plasma-metal reaction method, Mater. Lett. **64** (2010) 2575–2577.

[27] X. Liu, X. Piao, Y. Wang, S. Zhu, H.He, Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol, Fuel **87** (2008) 1076–1082.

[28] S. Gryglewicz, Rapeseed oil methyl esters preparation using heterogeneous catalysts, Bioresour. Technol. **70** (1999) 249–253.

[29] D. Veilleux, N. Barthelemy, J.C. Trombe, M. Verelst, Synthesis of new apatite phases by spray pyrolysis and their characterization, J. Mater. Sci. **36** (2001) 2245––2252.

[30] P.-L. Boey, G.P. Maniam, S.A. Hamid, Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: A review, Chem. Eng. J. **168** (2011) 15–22.

[31] F.X. Yang, Y.Q. Su, X.H. Li, Q. Zhang, R.C. Sun, Prepar–ation of biodiesel from *Idesiapolycarpa* var. vestita fruit oil, Ind. Crop. Prod. **29** (2009) 622–628.

[32] M. Kouzu, M. Umemoto, T. Kasuno, M. Tajika, Y. Aihara, Y. Sugimoto, J. Hidaka, Biodiesel production from soy–bean oil using calcium oxide as a heterogeneous catal–yst, J. Jpn. Inst. Energy **85** (2006) 135–141.

[33] K. Tanabe, Solid acid and bases, Kodansha, Tokyo, 1970, p. 53.

[34] H. Miura, K. Sugiyama, S. Kawakami, T. Aoyama, T. Matsuda, Selective hydration of acrylonitrile on metal oxide catalysts, Chem. Lett. **2** (1982) 183–186.

[35] K. Prepsch, S. Seibl, Tables for identification of the organic compounds by means of spectroscopy methods. Chemistry in Industry, Zagreb, 1982 (in Croatian).

[36] K. Tanabe, New solid acids and bases, Stud. Surf. Sci. Catal. **51** (1989) 27.

[37] A. Demirbas, Comparison of transesterification methods for production of biodiesel from vegetable oils and fats, Energy Convers. Manage **49** (2008) 125–130.

[38] S. Pleanjai, S.H. Gheewala, S. Garivait, Greenhouse gas emissions from production and use of used cooking oil methylester as transport fuel in Thailand, J. Clean. Prod. **17** (2009) 873–876.

[39] V.J. Gerpen, C.L. Peterson, C.E. Goering, Biodiesel: an alternative fuel for compression ignition engines, in:

ASABE distinguished lecture series No. 31, American Society of Agricultural and Biological Engineers, St. Joseph, MI, 2007.

[40] J. Lopes, L. Boros, M. Krahenbuhl, A. Meirelles, J. Daridon, J. Pauly, Prediction of cloud points of biodiesel, Energ. Fuel. **22** (2008) 747–752.

[41] JUS EN 14214:2004. AJUS EN 14214:2004. Automotive fuels. Fatty acids methyl esters for diesel engines-requirements and test methods. Belgrade, Serbia: Standardization Institute, 2004.

[42] Y. Katayama, Y. Tamaura, Development of new green-fuel production technology by combination of fossil fuel and renewable energy, Energy **30** (2005) 2179–2185.

[43] M.D. Tomić, L.Đ. Savin, R.D. Mićić, M.Đ. Simikić, T.F. Furman, Effects of fossil diesel and biodiesel blends on the performances and emissions of agricultural tractor engines, Thermal Science **17** (2013) 263–278.

IZVOD

Značaj strukturnih karakteristika CaO katalizatora za proizvodnju biodizela: Uticaj na smanjenje emisije gasova staklene bašte

Radomir B. Ljupković[1], Radoslav D. Mićić[2], Milan D. Tomić[3], Niko S. Radulović[1], Aleksandar Lj. Bojić[1], Aleksandra R. Zarubica[1]

[1]*Departman za hemiju, Prirodno–matematički fakultet, Univerzitet u Nišu, Niš, Srbija*
[2]*NTC NIS Naftagas – Novi Sad, Novi Sad, Srbija*
[3]*Poljoprivredni fakultet, Univerzitet u Novom Sadu, Novi Sad, Srbija*

(Naučni rad)

U ovom radu je ispitivan uticaj fizičko–hemijskih svojstava serije CaO katalizatora aktiviranih na različitim temperaturama za proizvodnju biodizela. Pomenuti katalizatori daju različite prinose u reakciji transesterifikacije triglicerida sa metanolom. Utvrdili smo bitnu povezanost između strukturalnih svojstava (tip poroznog sistema, tipična CaO kristalna faza i veličina kristalita do 25 nm, minimalni procenat kristalne faze CaO, ukupna baznost i potencijalno postojanje dve vrste baznih centara) CaO katalizatora pripremljenog i aktiviranog termijskim tretmanom na najvišoj temperaturi i katalitičke efikasnosti. Prednosti korišćenja ovog katalizatora su: kratko kontaktno vreme, standardna radna temperatura i atmosferski uslovi, relativno mali molski udeo reaktanata i mala količina katalizatora. Sve navedeno rezultiralo je veoma visokim prinosom biodizela visokog stepena čistoće. Svojstva različitih namešanih biodizel (dobijenog korišćenjem sintetisanog CaO katalizatora) goriva sa drugačijim udelima dizel i biodizel goriva ukazuju da što je veći udeo biodizela, bolja su ostvarena svojstva goriva imajući u vidu referentne EU standarde. Značajno smanjenje emisija CO_2 i CO gasova, i gotovo neznatno povećanje NO_x emisija, registrovano je kada je upotrebljeno gorivo sa povećanim udelom biodizela. Korišćenje namešanih goriva sa biodizel gorivom, kao i potencijalna totalna zamena fosilnih goriva sa biodizelom kao obnovljivim, alternativnim, ekološki prihvatljivim gorivom za dizel motore, moglo bi u velikoj meri da utiče na smanjenje emisije gasova koji izazivaju efekat "staklene bašte". Smanjenje emisije CO_x i NO_x gasova je od ogromnog značaja imajući u vidu da one izazivaju globalno zagrevanje. Buduća istraživanja na ovu temu i slično orijentisane mogla bi dati odgovor na savremene energetske zahteve i potrebe transporta u Srbiji, korišćenjem novog, alternativnog, obnovljivog izvora. Korišćenje biodizela obezbeđuje nezavisnost u pogledu uvoza sirove nafte, kao i brojne energetske, ekološke, geo-političke i ekonomske benefite.

Ključne reči: CaO katalizator • Emisija gasova koji izazivaju efekat "staklene bašte" • Proizvodnja biodizela • Strukturalna katalitička svojstva